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Advances in Atmospheric Chemistry Modeling: The LLNL IMPACT Tropospheric/ Stratospheric Chemistry Model

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Advances in Atmospheric Chemistry Modeling: The LLNL IMPACT tropospheric/stratospheric chemistry model

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Abstract

We present a unique modeling capability to understand the global distribution of trace gases and aerosols throughout both the troposphere and stratosphere. It includes the ability to simulate tropospheric chemistry that occurs both in the gas phase as well as on the surfaces of solid particles. We have used this capability to analyze observations from particular flight campaigns as well as averaged observed data. Results show the model to accurately simulate the complex chemistry occuring near the tropopause and throughout the troposphere and stratosphere.

Introduction

Accurate global modeling of atmospheric chemical species requires the correct simulation of many physical, chemical and dynamical processes, including convection, advection, tropospheric and stratospheric chemistry, emissions, deposition, aerosol microphysics and chemistry, radiative processes, and cloud processes. Many research studies over the last few decades have shown that such processes influence the regional and global distributions of aerosols and greenhouse gases and are important in the determination of current and projected climate change. Strong evidence exists that human activities have changed the chemical and thermal structure of the atmosphere (WMO/UNEP 1989, 1991, and 1995), affecting global climate. There have been sizable measured increases in the concentrations of carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and chlorofluorocarbons (CFCs) that can be linked to energy production and use (Wuebbles and Edmonds, 1992). CFCs have been linked to global ozone (O_3) depletion (Stolarski *et al.*, 1991; Gleason *et al.*, 1993) and are believed to be responsible for the observed stratospheric ozone loss in the Antarctic region (Farman *et al.*, 1985; Solomon *et al.*, 1986, 1988). In addition, as subsonic air traffic increased during the 1970s - 1990s, large amounts of nitrogen oxides (NO_x), sulfur oxides (SO_x), water vapor (H_2O), carbon monoxide (CO), hydrocarbons, soot, and CO_2 were emitted and may have affected ozone in the middle and upper troposphere - a region where ozone change has climatic importance. Understanding these issues involves a combination of observational campaigns, laboratory studies, and theoretical/modeling studies.

Past modeling studies have typically separately dealt with the troposphere and stratosphere. In tropospheric models, the stratosphere is seen as a boundary condition; and likewise, for stratospheric models, the complex physics of the troposphere are highly parameterized to simply provide the correct fluxes of species into its domain. This was done primarily to reduce the computational intensity and because it was thought that the two regions were distinct. However, there is a growing realization that the region of the tropopause (the thin region separating the troposphere and stratosphere) is highly important to climate prediction and unknown with respect to chemical processes. Under different support, LLNL had developed a stratospheric chemistry model, IMPACT. The goal of this project was to advance that model to include the chemistry and physics of both the troposphere and stratosphere and then validate model results to observations. The following sections describe the IMPACT chemical-transport-deposition model and then provide validation studies.

IMPACT Model Description

The LLNL (Lawrence Livermore National Laboratory) IMPACT (Integrated Massively Parallel Atmospheric Chemical Transport) model is a global, three-dimensional chemistry-transport-deposition model that contains both a prognostic troposphere and stratosphere. It uses as input meteorological fields from either a General Circulation model (GCM) or data assimilated meteorological fields (Rotman et al., 1993; Penner et al. 1998). The data assimilated meteorological fields are currently those from the Data Assimilation Program at NASA-Goddard. This data is assimilated output from the DAO based GEOS system that covers the time period of the ongoing NASA STRAT measurement campaign from May 1995 to present (and should continue for some time into the future). The meteorological data is provided on a 2 degree by 2.5 degree horizontal resolution with 46 levels in the vertical, from ground to 0.1 mb. This data contains a more highly defined boundary layer than previous tropospheric models and the resolution allows for analysis of either regional to global scale and tropospheric to stratospheric issues. The advantage of using assimilated data is that the model can simulate specific historic events, allowing direct model-observation comparisons and thus model validation.

IMPACT is based on an operator splitting method for advection, diffusion, convection, photolysis and chemistry. The chemistry equations are solved using SMVGEAR II (Jacobson, 1995), a highly optimized version of the original predictor/corrector, backward differentiation code of Gear (1971) that uses a variable time step, variable order, implicit technique for solving stiff numerical systems with strict error control. The chemical continuity equation is solved for *each individual species* (i.e., no lumping of species into chemical families are made). The chemical reaction mechanism and applicable parameters are incorporated in files that are generated external to the IMPACT model, making changes to the mechanism straightforward.

The photochemistry includes reactions for both the stratosphere and troposphere. Reactions appropriate for the stratosphere include those for the families O_x, NO_y, ClO_y, HO_y, BrO_y, and CH_4 and its oxidation. The model also accounts for methane-produced water vapor in the stratosphere. Reactions appropriate for the troposphere are based on the mechanism of Lurmann et al., 1986. The mechanism has been updated to account for isoprene reactions (Paulson and Seinfeld, 1992), reactions in the remote atmosphere (Jacob and Wofsy, 1988) and peroxy radical reactions (Kirchner and Stockwell, 1996). Species treated include O_3, OH, PAN, NO, NO_2, CO, CH_4, HNO_3, isoprene, ethane, propane, C4-5 alkanes, C6-8 alkanes, ethene, propene, ketones (including acetone), formaldehyde, acetaldehyde, and higher aldehydes. Where applicable, absorption cross sections and reaction rate coefficients were taken from DeMore et al., 1997. Many of the isoprene reactions have been updated to reflect state-of-the-art knowledge (Connell and Atherton, 1999). Results of recent laboratory kinetic studies on higher hydrocarbon oxidation steps and their implications for rate constants for homologous reaction have also been incorporated (e.g., deGouw and Howard, 1997). A simplified version of the chemical mechanism also exists for use with IMPACT. It allows for much faster computational speed (and can be used for extremely long simulations, if required).

Advection in all three directions uses a variable order multidimensional flux form of the semi-Lagrangian method, an up-stream-biased monotonic grid point scheme (Lin and Rood, 1996). The upstream nature of this method reduces phase errors to a minimum and the monotonicity control eliminates the need for a filling algorithm and the severe problems that would arise with negative values of chemical species concentrations. This scheme also avoids the strict Courant stability problem at the poles, thus allowing large time steps to be used, resulting in a highly efficient advection operation. Vertical diffusion is done implicitly following the algorithm of Walton et al. (1988). Convective transport uses the scheme of Lin (DAO, NASA Goddard, private communication), which for infinitely thin layers is essentially the apparent momentum transport of clouds (Schneider and Lindzen, 1976).

IMPACT uses the dry deposition algorithm of Wang et al. (1998). This is an improved version of that published in Jacob et al. (1993). This algorithm internally computes the local deposition velocity for a tracer species based on aerodynamic resistance and surface resistance, (Wesely et al., 1985). For this COSAM Rn/Pb exercise, both species were dry deposited, Rn as a gas and Pb as an aerosol. Wet scavenging has four separate components:

- *convective wet deposition* (Balkanski et al. 1993) - treats the deposition due to convective updrafts. This uses the values of convective mass flux in the GEOS-STRAT data.
- *large scale (stratiform) scavenging* (Giorgi and Chameides 1986) - requires separate condensation rates for large scale and convective precipitation, yet our GEOS-STRAT meteorological data files contain a single condensation rate. The GEOS-STRAT data does include both total convective and large scale precipitation reaching the surface. We use this data to partition the entire column of condensation rates into convective and large scale components. This model then calculates the rate at which these aerosols or gases are incorporated into raindrops within the cloud.
- *large scale washout* - washout by large scale precipitation in grid boxes below cloud is computed as a first order loss process applied to the precipitating fraction (F) of the grid box (defined by the maximum value of F in the overhead grid boxes). The 3D field of large scale precipitation is calculated using the 3D condensation rate along with the 2D fields of convective and large scale precipitation reaching the surface. A washout rate constant of 0.1 (mm^{-1}) normalized to the precipitation rate was used.
- *convective scavenging* (Giorgi and Chameides 1986) (Koch et al. 1996) - similar to large scale scavenging but uses the fraction of the condensation rate from convective processes as determined by the 2D fields of convective and large scale precipitation reaching the surface. Also, when calculating F (the fraction of the grid box where precipitation takes place), uses different estimates for F0 (the maximum value of F, L (the cloud liquid water content), Tc (the duration of the precipitation event), and beta_min (the minimum value for the rate of conversion of cloud water to precipitation).

Photolysis rates are obtained by a clear-sky lookup table developed using methodologies in Douglass et al., 1997. Normalized radiative fluxes calculated from the model of Anderson et al. (1995) are tabulated as a function of wavelength, solar zenith angle, overhead ozone and pressure. Temperature dependent molecular cross sections, quantum yields, and solar flux are tabulated separately. Rates are adjusted in the troposphere depending on the presence of clouds and the archived cloud fraction. This adjustment is done to correctly mimic OH levels and methyl chloroform lifetimes. Heterogeneous reactions with rates that depend on gas-particle collision rates, such as the hydrolysis of N_2O_5, are easily included. This approach can capture the gross features of polar stratospheric heterogeneous chemistry.

Given the completeness of the physics and mathematics and its high resolution, simulations with the IMPACT model are computationally intensive. For this reason, IMPACT has been developed and implemented on massively parallel computers such as the Cray T3E and the IBM SP2 (it also runs on Cray C and J90's, workstations and other massively parallel computers). The ability to compute on parallel machines has greatly advanced our throughput capabilities. With approximately 100 species and a $2° \times 2.5°$ horizontal resolution with 46 levels, a one year simulation requires roughly 400 hours on 121 processors of a T3E-900. (This same simulation would require roughly 5,000 hours on a single Cray C-90 processor.) At $4° \times 5°$ resolution, the computational time on the T3E-900 is 60 hours. This model was also used in the DOE-PATHFORWARD project in collaboration with COMPAQ computer. COMPAQ ported IMPACT to their new Quadrics connected parallel platform. Results show performance to be very good; nearly 2 ½ times faster that the Cray T3E-900.

We are presently developing a chemistry model which will treat gas phase sulfur reactions using prognostic O_3, NO_3, and OH. We will also include models for heterogeneous stratospheric sulfur reactions as well as aqueous sulfur reactions in the troposphere.

IMPACT model applications and evaluation

Previously, the IMPACT model has been used to study stratospheric distributions of chemical species and tracer distributions in the stratosphere (Rotman et al., 1993). The IMPACT model was also used in a budget study of upper tropospheric NO_x (Penner et al., 1998). This study used an earlier version of IMPACT to quantify the contributions to the NO_x cycle from in-situ sources (lightning and aircraft emissions), convection from the surface (fossil fuels, biomass burning and soils), stratospheric transport and photochemical recycling of nitric acid (Penner et al., 1998). Comparing predictions from IMPACT and the GRANTOUR global model showed the major difference in NO_x budgets resulted from different treatments of vertical transport, especially convection. Additionally, accurately defining the tropopause also affected model results.

The IMPACT model was also used to simulate the ^{222}Rn and ^{210}Pb cycles, as part of our participation in the Comparison of the Performance of Large Scale Models in Simulating Atmospheric Sulphate Aerosols (COSAM) (Bergmann et al., 1998). This international comparison study convened in Halifax, N.S., in October 1998. It was a follow-up to recent WCRP workshops on the transport and scavenging of tracers (e.g. CFC-11 and ^{222}Rn). Figure 1 shows the IMPACT predicted June-July-August average mixing ratios for (a) ^{222}Rn at pressure = 300 hPa and (b) zonal average ^{222}Rn. Our model predicted ^{222}Rn compares favorably with other models (Barrie et al., 1999; Lohmann et al., 1999), although IMPACT may have stronger convection in the upper troposphere than others.

More recently, the IMPACT model has been used to study the photochemical cycles important in the upper troposphere and lower stratosphere. The results have been compared with measurements from aircraft sampling campaigns. Specifically, an IMPACT simulation driven by the meteorological fields from autumn 1997 was compared to results from NASA's SONEX campaign, flown over the North Atlantic during the same time period (fall 1997) (Atherton et al., 1998). SONEX addressed the role of lightning and aircraft NO_x on upper tropospheric and lower stratospheric air composition (see, e.g., Chatfield et al., 1999; Jaegle et al., 1999; Singh et al., 1999; Thompson et al., 1999). The SONEX mission consisted of roughly 14 flights during October and November 1997. The IMPACT model simulation period began on June 1, 1997. The results discussed below are from two sampling days during October 1997.

Figure 2 shows the IMPACT predictions and SONEX O_3 observations for flight #3 on October 13, 1997. This flight extended from NASA Ames, California to Bangor, Maine. Both IMPACT and the UV-DIAL observations (Browell, pers. comm., 1999) show the presence of strong stratospheric influence at longitudes between 90W and

100W. This influence is seen as low as 4–6 km, well into the troposphere. The IMPACT model reproduces not only the location, but also magnitude of this phenomenon.

Figure 3 shows the IMPACT predicted results for October 15, 1997, along with the ozone distributions obtained using UV-DIAL sampling techniques (Browell, pers. comm., 1999) on SONEX flight #4 (also October 15, 1997). Flight #4 traversed the North Atlantic, from Bangor, Maine to Shannon, Ireland, at latitudes of 53 - 57°N. Plotted in the same figure are the IMPACT results for 56°N. The model predicts a strong stratospheric O_3 influence in the same region as the UV-DIAL observations. As before, the model reproduces well the location and concentrations of ozone associated with this stratospheric influence.

Figure 4 plots monthly average October 1997 IMPACT profiles for a number of species, along with measurements from two different aircraft campaigns, TRACE-A and PEM-Tropics. Because the model results are for a different year than the sampling campaigns, an identical comparison should not be expected. Some generalities, however, may be identifiable. In Figure 4a, the IMPACT model reproduces fairly well the profiles of O_3, C_3H_8, PAN, and CH_3OOH. IMPACT also predicts well the structure of the NO_x, CO, and C_2H_6 profiles, although the model concentrations are slightly less than the measurements. The model-predicted concentrations of a number of species at the surface are slightly lower than the measurements, but that may depend on the particular amount of biomass burned during the sampling campaign, the role of local convective events, etc.

In Figure 4b, the model predicts distributions of O_3, NO_x, CO, H_2O_2, PAN, and CH_3OOH that are similar to observations (although O_3 tends to be too high above 6km). The model predicts higher O_3 than measured in the upper troposphere, but that again may depend on synoptic meteorological events. The model tends to underpredict C_2H_6 and C_3H_8. As occurs in a number of models, the predicted HNO_3 concentrations are higher than observed, possibly due to a process that converts HNO_3 to NO_x but is not represented in current models.

Conclusion

We have developed and applied the IMPACT chemistry-transport-deposition model. It provides the capability to simulate the distribution of important trace species throughout the troposphere and stratosphere. Applications show the model to accurately simulate the vertical and horizontal distribution of many important trace species, in particular ozone, throughout the entire extent of the atmosphere. Some issues remain. The model produces somewhat high levels of ozone in the upper troposphere and high values of nitric acid throughout the atmosphere; these will be investigated further. This modeling capability will provide the central tool for continued analysis of atmospheric chemistry and the important links of chemistry to climate change.

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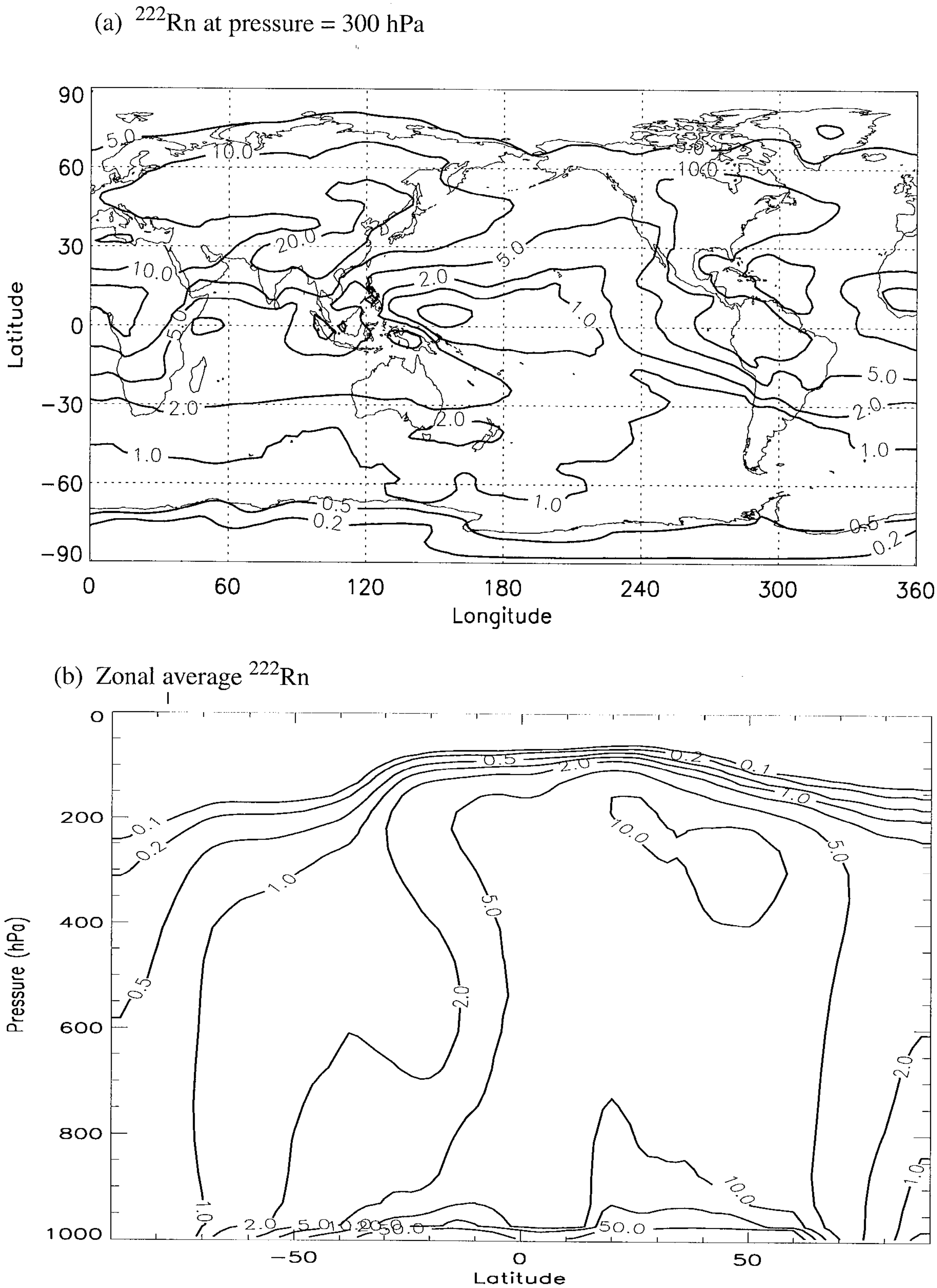


Figure 1. IMPACT model predictions of ^{222}Rn for June-July-August, in units of 1×10^{-21} mol/mol, (a) pressure = 300 hPa and (b) zonal average.

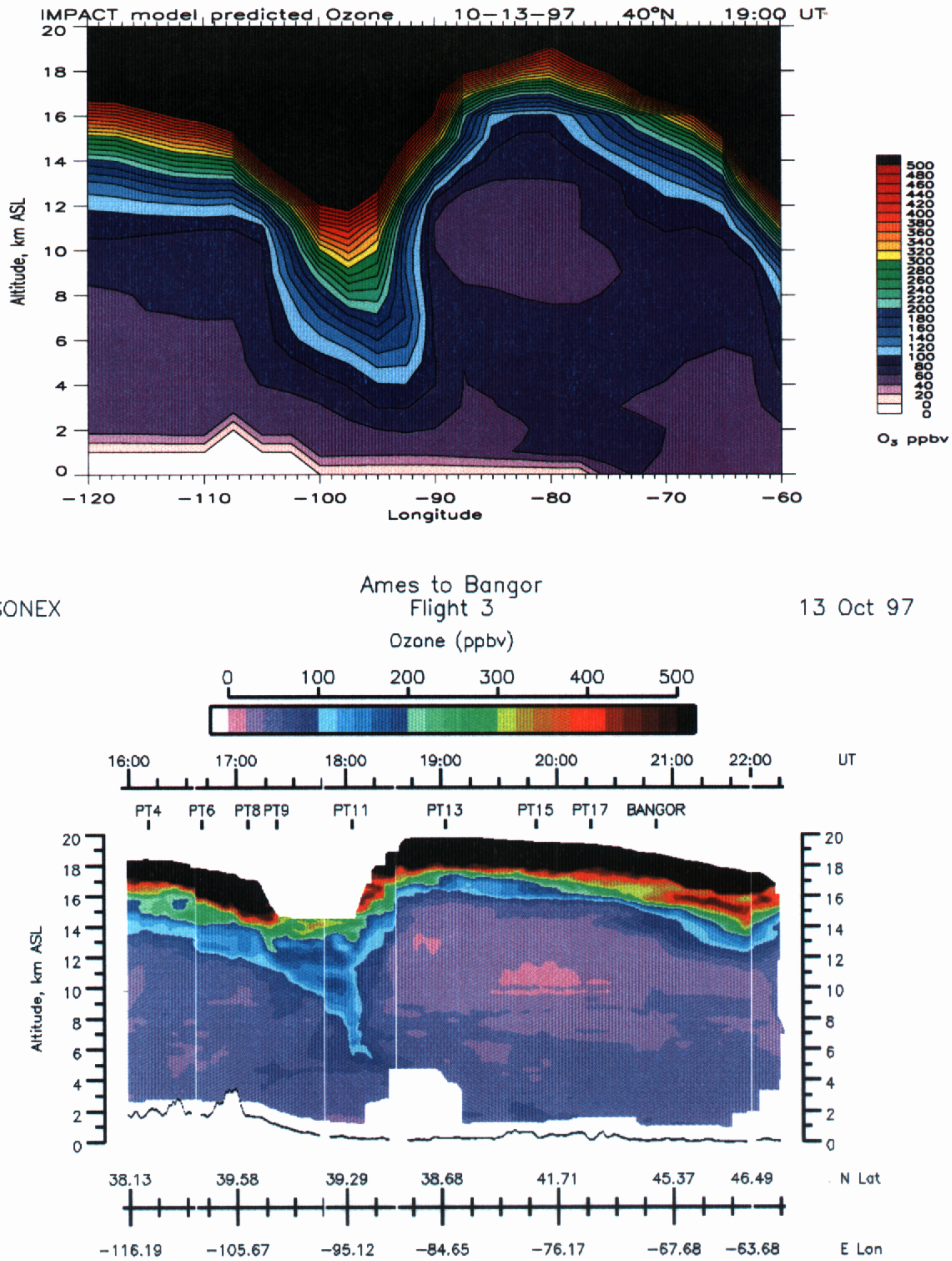


Figure 2: IMPACT model prediction 10-13-97 19:00 UT (upper), compared to SONEX flight #3, Ames to Bangor 10-13-97 cross-continent sampling at ~11 km (lower).
Mission summary notes "... With exception of air masses near storm system (... near Misissouri at 95W) ... air over continent was clean. West of storm system ozone=60-65 ppb..."

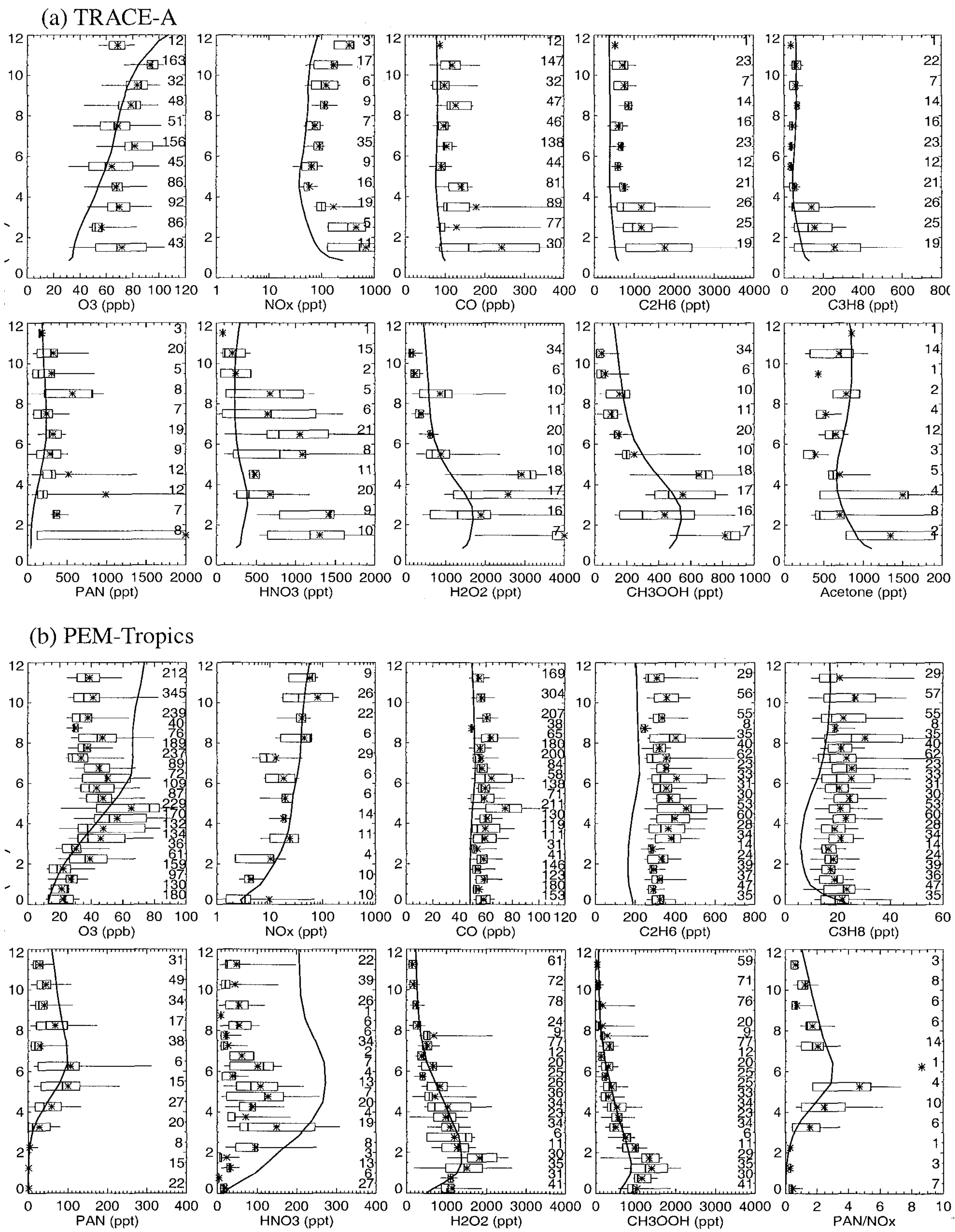
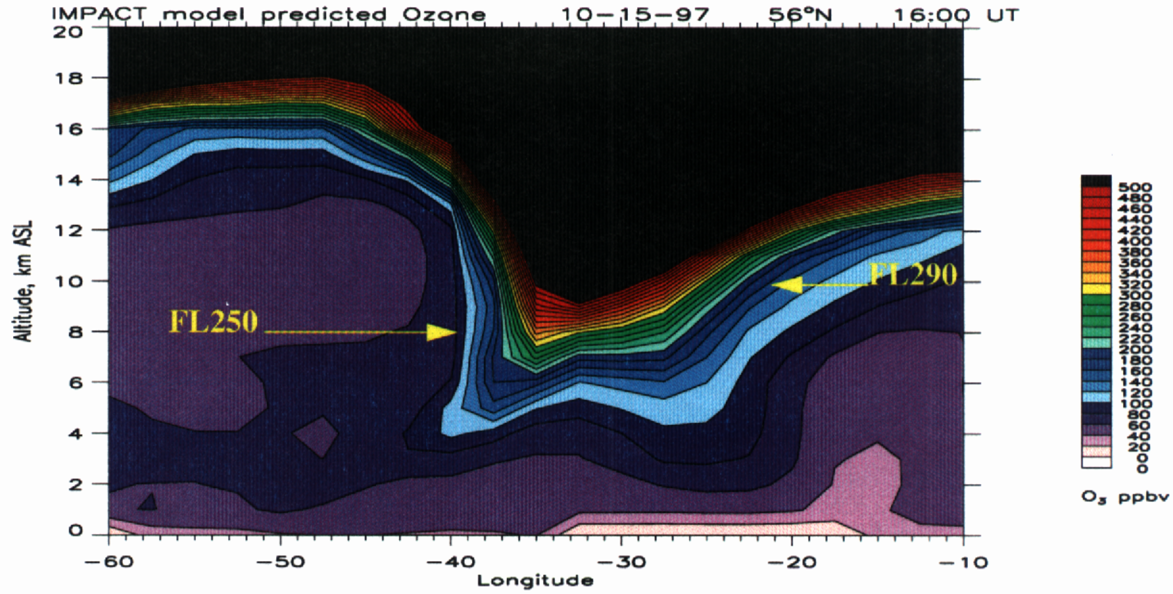


Figure 4. IMPACT predicted October 1997 average concentrations (solid lines) for a number of species plotted with measurements (symbols) from (a) TRACE-A (Africa, Sept./Oct. 1992, Fishman et al., 1996) and (b) PEM-Tropics (Tahiti, Aug/Sept. 1996, Hoell et al., 1999).



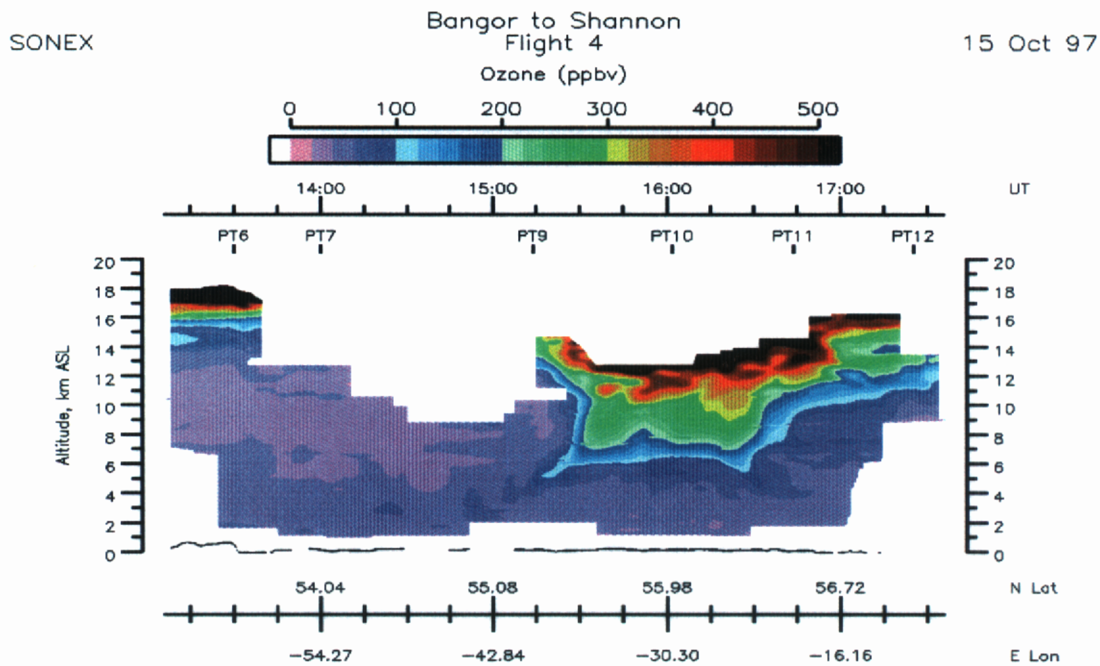


Figure 3 : IMPACT model prediction 10-15-97 16:00 UT (upper), compared to SONEX flight #4 10-15-97, Bangor to Shannon (lower).

Mission Summary notes that, "... At 15:03, begin ascent to FL250, which was inside inversion - O3>250 ppbv, ... At 20W, at FL290, tropospheric air masses resume..."